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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	1978
number	Supplement
page range	37-42
year	1978
URL	http://hdl.handle.net/10097/27948

Supplement to Sci. Rep. RITU, A, June, 1978

CRYSTALLIZATION OF AMORPHOUS Si AND Ge PREPARED ON Si(111) AND Ge(111) SURFACES BY ARGON ION BOMBARDMENT

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ABSTRACT

Amorphous thin layers have been formed on Si(111) and Ge(111) clean surfaces by argon ion bombardment and the recovery process of the layers has been in-situ observed by means of reflection high energy electron diffraction (RHEED). When amorphous layers, 40 Å or more in thickness, are annealed, a complex structure containing a lot of {111} twins first occurs on the way of the recovery and then changes to a single crystal surface with a good flatness on the atomic scale.

INTRODUCTION

It is well known that bombardment of crystal surfaces with fast ions of tens or hundreds KeV heavily disturbes an atomic arrangement near the surface and roughes the surface, leading the structure to an amorphous state. Conversion of crystalline Ge to amorphous Ge by bombardment with 100 KeV O^- ions was in-situ observed by means of transmission electron microscope and mechanism of the conversion was discussed in details [1]. Recrystallization of amorphous Si layer produced on Si(111) surface by bombardment with 50 KeV Ar^+ ions was recently studied by Ohdomari and Onoda [2] and the structure of amorphous Si layer on crystalline Si after annealing was analysed to be composed of multiply twinned particles [3]. These amorphous layers so far studied were 100-1000 Å thick.

On the other hand, it is said that the bombardment with argon ions of a low energy of 100-1000 eV, which is a standard method to clean crystal surface, also changes the surface to be in an amorphous state, since reflection spots in the low energy electron diffraction (LEED) pattern disappears when the argon ion bombardment is carried out. The disappearance, however, does not necessarily mean that the structure is amorphous, because no reflection spot is observed in the LEED pattern of a very rough surface. In order to study whether structure on surface is changed to be in an amorphous state by argon ion bombardment and how the structure recovers to a single crystal having a flat surface on the atomic scale by high temperature annealing, structure changes on Si(111) and Ge(111) surfaces caused by argon ion bombardment and the recovery process on annealing have been in-situ observed by means of reflection high energy electron diffraction (RHEED).

EXPERIMENTAL

Mirror polished (111) surfaces of n-type silicon and germanium with the resistivity of 200 Ω cm and that of 40 Ω cm, respectively, were chemically etched before being placed in a RHEED apparatus. The details of the apparatus were already reported by Ino [4]. Cleaning of the Si(111) and Ge (111) surfaces were carried out by high temperature heating and by argon ion bombardment followed by high temperature annealing, until reflection spots of Si(111) 7 x 7 and Ge(111) 2 x 8 superstructure were clearly observed in the respective RHEED patterns. The temperature of the crystal surface was measured for temperatures less than 800°C by an infra-red pyrometer and for higher temperatures by an optical pyrometer. The background pressure in the apparatus was $\sim 10^{-10}$ Torr. The diffraction pattern was observed under the accelerating voltage of 20 KV.

RESULTS AND DISCUSSION

Figure 1 is a RHEED pattern of Si(111) surface after cleaning. Sharp reflection spots due to the 7 x 7 super-structure are clearly observed in the pattern. When a gentle argon ion bombardment (500 V, ~ 0.3 μA cm^{-2}) was carried out at room temperature (RT), the reflection spots rapidly became weak, the spot size remaining unchanged, and on the contrary diffuse fundamental reflection spots due to the bulk structure bellow surface became strong and background intensity increased, as shown in Fig. 2. These suggest that the structure on the surface is not only disordered, but also the surface is roughed by the bombardment, and that the diffraction pattern changes from a reflection type to a transmission one with increasing roughness of the surface. When the argon ion bombardment was further continued, the diffuse bulk reflection spots, Kikuchi lines and Kikuchi bands gradually disappeared in the strong background, and at last, a few diffuse halos characteristic of amorphous structure were distinctly observed near the shadow edge. The argon ion current in the present experiment was chosen to ~ 0.3 μAcm^{-2} less than those, 1-100 μA cm^{-2} [5], often used in argon ion bombardment experiment, because argon ion bombardment with small current slowly damaged the surface. An intense argon ion bombardment (500 V, ~ 2 μA cm^{-2}) changed

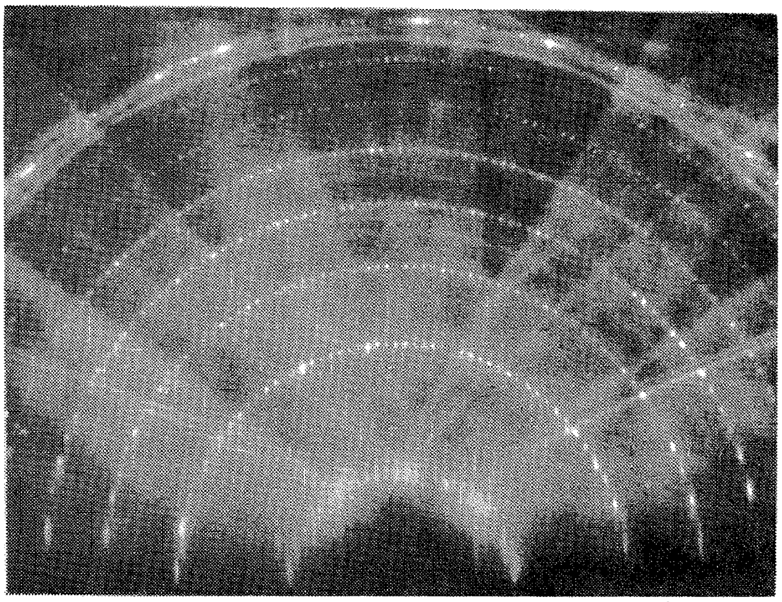


Fig. 1 RHEED pattern of Si(111) 7 x 7 structure. [1$\bar{1}$0] incidence.

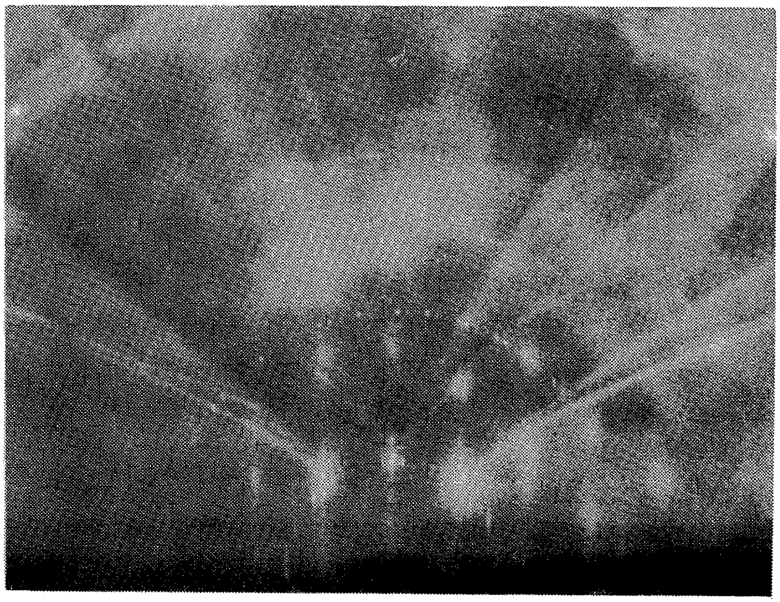
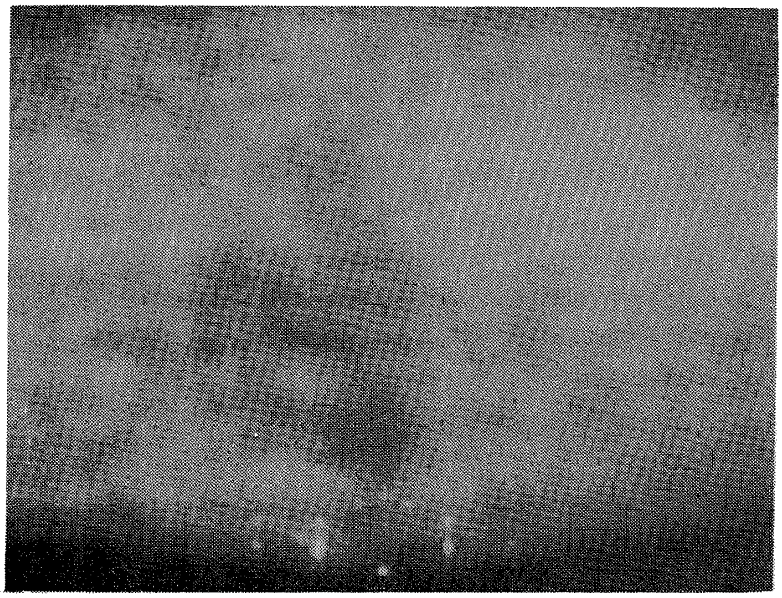


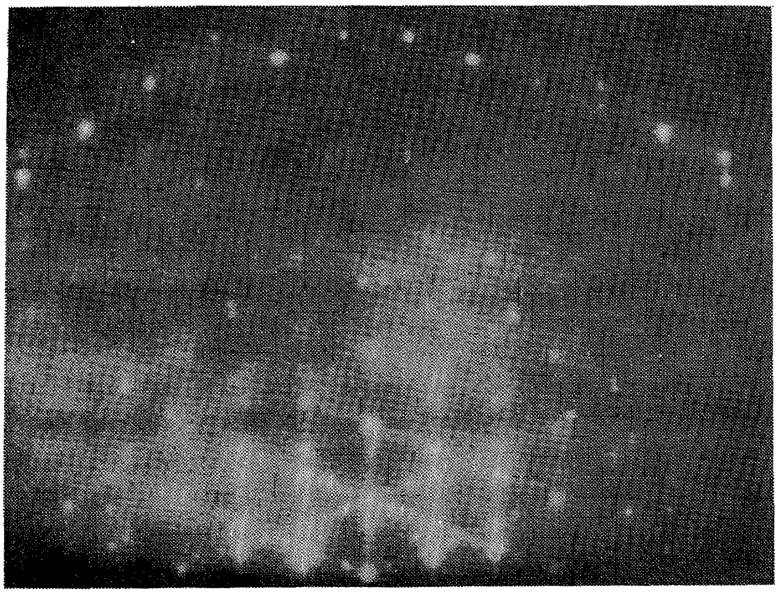
Fig. 2 RHEED pattern of Si(111) surface slightly damaged by argon ion bombardment. [1$\bar{1}$0] incidence.

the surface to the structure showing the halo pattern within a few minutes.

When the intense argon ion bombardment was continued for 10 min at RT, the Si(111) surface showed a diffraction pattern composed of a few diffuse halos and Kikuchi bands. The latter could faintly be seen only in the region far away from the shadow edge. The thickness, 40 Å, of damaged layer on the surface was roughly estimated from a good similarity in features to a diffraction pattern of Si(111) surface on which



(a)



(b)

Fig. 3 RHEED patterns of Si(111) heavily damaged surface during annealing. (a) begining of recovery and (b) formation of twin structure. $[1\bar{1}0]$ incidence.

a fixed amount of amorphous Si was deposited. When the temperature of the surface was raised stepwise, Kikuchi lines and bands indistinctly appeared around 510°C and after a while, some reflection spots gradually occurred near the shadow edge of the diffraction pattern, as shown in Fig. 3 (a). That is, recrystallization began and small Si grains of a diamond structure were formed in the heavily damaged layer. The grain size is estimated from the broadness of the reflection spots to be a few tens Å. With an increase of annealing time, the spots became strong and the background intensity decreased, as shown in Fig. 3 (b). This diffraction pattern is an electron diffraction pattern in a transmission case, which suggests that the surface was still rough in this stage. The strong spots in the pattern arise from Si grains having the same orientation as that of the bulk and from primary twins grown on (111) planes parallel to the surface. Most of weak spots can be explained by the other primary twins grown on the other {111} planes. In addition, there exist many diffuse streaks through the spots in the diffraction pattern. The streaks are considered to result mainly from small thickness of the twins. Namely, the twins seem to be microtwins. The details will be reported elsewhere. When annealing was further performed around 610°C, the twin spots became weak and a lot of sharp streaks due to the 7 x 7 superstructure occurred. These indicate that the microtwins coalesced to grains having the same orientation as that of the bulk and vanished, and that the surface became flat and the 7 x 7 superstructure was formed on it. Average size of the grains having the 7 x 7 superstructure as their surface structure is inferred from the elongation of the reflection spots due to the superstructure to be 100-200 Å. Heating at much higher temperature improved the structure on the surface and features in the diffraction pattern equaled that before argon ion bombardment. The recovery process of surfaces having thicker layer damaged was almost the same as that above described.

Layer, about 20 Å thick, heavily damaged was formed on Si(111) surface by carrying out argon ion bombardment (500 V, $\sim 1\ \mu A\ cm^{-2}$) at RT for 10 min. Kikuchi lines, Kikuchi bands and diffuse fundamental reflection spots were dimly seen in the strong background of the diffraction pattern. When the surface was annealed, streaks of fundamental reflections first appeared

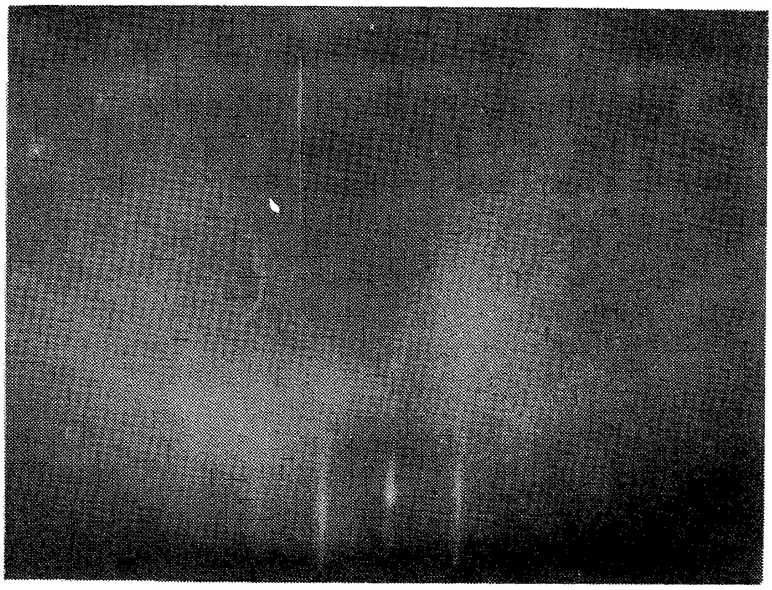


Fig. 4 RHEED pattern of Si(111) damaged surface at the begining of recovery. The damaged layer is thinner than that of the surface of Fig. 3. [1$\bar{1}$0] incidence.

near the shadow edge, as shown in Fig. 4, and after a while, streaks due to the 7 x 7 superstructure arose between the streaks in the background. Such streaks are characteristic of reflection electron diffraction pattern resulting from a flat surface. In this case, no twin spot was observed on the way. Such a behavior in the recovery process was seen also in Si(111) surface slightly bombarded. These suggest that the Si(111) surface having thin damaged layer recovers directly to a flat single crystal surface without formation of twins.

Ge(111) surface was bombarded with argon ions, and subsequently, annealing was carried out. The recovery happened around 300°C lower than 510°C in Si(111) surface, but general feature of the recovery process was the same as that of Si(111) surface.

When thin amorphous Si film was deposited 40 Å thick on Si(111) clean surface and annealed in a vacuum of $\sim 10^{-10}$ Torr, the RHEED pattern changed to a pattern in which a lot of diffraction spots due to {111} microtwins were observed. Features of the pattern was almost the same as those of Fig. 3 (b). Such pattern was, however, not seen in amorphous Si films thinner than about 20 Å in thickness. Thus, the growth of the twins seems to be closely related not to the surface roughness induced by argon ion bombardment but to the thickness of damaged layer. Damaged layer thicker than 40 Å is considered to be necessarily produced on Si and Ge surfaces whenever an intense argon ion bombardment [5] with an ion current of 10-100 $\mu A\ cm^{-2}$ is carried out for 20-30 min. Therefore, it can be said from the present observation that Si(111) and Ge(111) surfaces bombarded with argon ions for the sake of their cleaning grow a transitive complex structure containing a lot of {111} microtwins on the way of annealing and next recover to a single crystal surface with a good flatness on the atomic scale.

This work is supported in part by the fund from the Ministry of Education in Aid of Projected Research on Amorphous Materials.

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